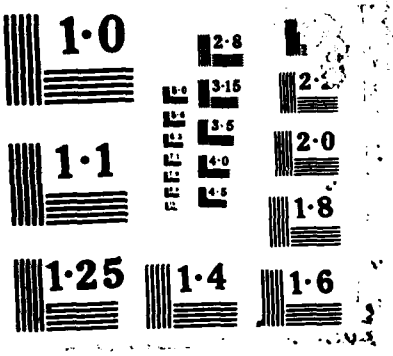
AD-A191 642 ELECTRONIC AND IONIC TRANSPORT IN POLYMERS(U) TEXAS UNIV AT ARLINGTON DEPT OF CHEMISTRY T D SHAFFER 06 APR 88 N00014-86-K-0769 1/1

UNCLASSIFIED F/G 7/6 NL


1·0
1·1
1·25
1·4
1·6
2·0
1·8

(4)

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION / AVAILABILITY OF REPORT Unlimited
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report No. 5	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION The University of Texas at Arlington 6b. OFFICE SYMBOL *(If applicable)*	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research
6c. ADDRESS *(City, State, and ZIP Code)* Department of Chemistry, Box 19065 The University of Texas at Arlington Arlington, Texas 76019	7b. ADDRESS *(City, State, and ZIP Code)* 800 North Quincy Street Arlington, Virginia 22217
8a. NAME OF FUNDING / SPONSORING ORGANIZATION Defense Advanced Research Projects Agency 8b. OFFICE SYMBOL *(If applicable)* DARPA	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-86-K-0769
8c. ADDRESS *(City, State, and ZIP Code)* 1410 Wilson Boulevard Arlington, Virginia 22209	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. | PROJECT NO. | TASK NO. | WORK UNIT ACCESSION NO.

11. TITLE *(Include Security Classification)*
Electronic and Ionic Transport in Polymers

12. PERSONAL AUTHOR(S) Martin Pomerantz, John R. Reynolds, Krishnan Rajeshwar, Dennis S. Marynick, Timothy D. Shaffer

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT *(Year, Month, Day)*	15. PAGE COUNT
Quarterly-Technical	FROM 1/1/88 TO 3/31/88	1988 April 6	4

16. SUPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*
FIELD	GROUP	SUB-GROUP	Electronically conducting polymers.

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

Ethylmercapto-substituted polythiophenes have been studied and when doped, they show considerably lower conductivity than the parent polythiophene. Calculations have shown that a significant fraction of the positive charge resides on the sulfur of the side chain and this is consistent with the low conductivity. Mechanistic electrochemical studies on these systems have been completed. Studies have continued on the fluorescence modulation induced by the redox switching of polypyrrole. A pyrrole substituted at the 3-position with anthracene has been prepared and characterized. A new soluble, electroactive polymer, poly(bis-oxystyryldithiolene nickel) has been prepared and is being studied. A quartz crystal microbalance study of the electropolymerization of pyrrole has been completed and shows this is a useful quantitative tool for polymer deposition studies. A PMO study of aromatic conducting hydrocarbon oligomers and polymers has been completed.

DISTRIBUTION STATEMENT A
Approved for public release; Distribution Unlimited

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. JoAnn Millikan	22b. TELEPHONE *(Include Area Code)* (202) 696-4410 | 22c. OFFICE SYMBOL

Technical Report

Principal Investigators: Martin Pomerantz, Grant Administrator, John R. Reynolds, Krishnan Rajeshwar, Dennis S. Marynick and Timothy D. Shaffer

Contractor: The University of Texas at Arlington

Telephone No. (817) 273-3811

Cognizant ONR Scientific Officer: Dr. JoAnn Millikan

Contract No.: N00014-86-K-0769

Short Title of Work: "Electronic and Ionic Transport in Polymers"

Reporting Period: January 1, 1988 - March 31, 1988

This is Technical Report No. 5 (1987-1988)

Description of Progress

Conductivity studies of oxidized complexes of poly(3-ethylmercaptothiophene) and poly(3,4-bis-ethylmercaptothiophene) yield maximum values of $2 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$ and $2 \times 10^{-7}\ \Omega^{-1}\ cm^{-1}$ respectively, while unsubstituted doped polythiophene has a value of $4 \times 10^{-1}\ \Omega^{-1}\ cm^{-1}$. Charge density calculations show that a significant fraction of positive charge appears to be on the ethylmercapto sulfur atom, accounting for the difference.

Electrochemical characterization of the ethylmercapto-substituted polythiophenes has been completed. The mechanistic aspects of the over oxidation (and passivation) of these compounds, as well as the parent polymers, have been elucidated via the combined use of FTIR and voltammetry. A manuscript detailing these results is in preparation.

In continuation of our ongoing studies on fluorescence modulations induced by redox switching of polypyrrole, attempts have been made to covalently anchor the fluorophore on the conducting polymer surface. The rationale is to effectively discriminate the emission from any fluorescing molecule situated beyond a critical (and controllable) quenching distance from the polymer surface. To this end, anthracene has been attached to the 3-position of thiophene. This new monomer has been characterized by elemental analysis, NMR, IR, electrochemical techniques, and fluorescence spectroscopy. Studies on the electropolymerization of this compound are in progress.

A collaborative project with researchers at General Dynamics has been initiated to study High Temperature Electroactive Composites. Polythiophene/bismaleimide composites are being examined for thermal stability and energy absorption characteristics.

A new soluble and electroactive transition metal ion containing polymer, poly(bis-oxystyryldithiolene nickel) has been prepared and shown to be semiconducting in the air oxidized form. Cyclic voltammetric analysis has been used to define the $[NiL_2]^{2-} \rightleftarrows [NiL_2]^{1-} \rightleftarrows [NiL_2]^{0}$ transitions.

A quartz crystal microbalance (QCM) study of the electropolymerization of pyrrole has been completed. This work shows the QCM can be used as a quantitative tool for polymer deposition. In addition, electrode surface, electrolyte and solvent effects have been correlated with the efficiency of electropolymerization/deposition.

A paper detailing the use of Perturbation Molecular Orbital theory (PMO), based on simple odd alternate hydrocarbon fragments and Hückel M.O. theory, to provide band gaps, ionization potentials and electron affinitives of aromatic conducting polymers, has been submitted for publication.

A special vacuum line has been custom designed and built for electrochemistry studies of air-sensitive compounds.

Personnel Changes

Dr. Sanjay Basak has joined our group as a Postdoctoral Research Associate. Robert Uitz has joined our group as a postgraduate research assistant.

Publications:

Paper Published

Tsai, E.; Jang, G-W.; Rajeshwar, K. "Proton Transport Accompanies Redox Switching of Polypyrrole: A Spectroelectrochemical Study," *J. Chem. Soc., Chem. Commun.*, 1776 (1987).

Wang, S.J.; Naidu, S.V.; Sharma, S.C.; De, D.K.; Jeong, D.Y.; Black, T.D.; Krichene, S.; Reynolds, J.R.; Owens, J.M. "High T_cSuperconductor $YBa_2Cu_3O_{7-\delta}$ Studied by Positron Annihilation," *Phys. Rev. B.*, **37**, 603 (1988).

Papers in Press

Panchalingam, V.; Reynolds, J.R. "Structure of the Alternating Copolymer of 1,3-Cyclohexadiene and Chloroacrylonitrile," *Macromolecules*, in press.

Martinez, M.; Reynolds, J.R.; Basak, S.; Black, D.A.; Marynick, D.S.; Pomerantz, M. "Electrochemical Synthesis and Optical Analysis of Poly[(2,2'-dithienyl)-5,5'-divinylene]," *J. Polym. Sci. Polym. Phys. Ed.*, in press.

Reynolds, J.R. "Electrically Conductive Polymers: Processible, Stable, and Useful," *Chemtech*, in press.

Tsai, E.W.; Pajkossy, T.; Rajeshwar, K.; Reynolds, J.R. "Anion Exchange Behavior of Polypyrrole Membranes," *J. Phys. Chem.*, in press.

Shaffer, T.D. "Phase Transfer Catalyzed Polymerization of α,α'-Dibromo–xylene Isomer," *J. Polym. Sci., Polym. Lett. Ed.*, in press.

Papers Submitted for Publication

Reynolds, J.R., Sundaresan, N.S.; Pomerantz, M., Basak, S., Baker, C.K. "Self-Doped Conducting Copolymers: A Charge Transport Study of Poly{pyrrole-co-[3-(pyrrol-1-yl)propanesulfonate]}," *J. Electroanal. Chem.*, submitted for publication.

Wang, F.; Reynolds, J.R. "Soluble and Electroactive Nickel Bisdithiolene Complex Polymers," *Macromolecules*, submitted for publication.

Baker, C.K.; Reynolds, J.R. "A Quartz Microbalance Study of the Electrosynthesis of Polypyrrole," *J. Electroanal. Chem.*, submitted for publication.

Mori, E.; Baker, C.K.; Reynolds, J.R.; Rajeshwar, K. "Aqueous Electrochemistry of Tellurium at Glassy Carbon and Gold: A Combined Voltammetry-Oscillating Quartz Crystal Microgravimetry Study," *J. Electroanal. Chem.*, submitted for publication.

Pomerantz, M.; Cardona, R.; Rooney, P. "The Application of the PMO Method to Aromatic Conducting Polymers," *Macromolecules*, submitted for publication.

Oral Presentations and Visitors

The following presentations were given by J. R. Reynolds:

Rockwell International Science Center, Thousand Oaks, CA, January 1988
"Structurally Modified Polymers with Controllable Electronic and Ionic Properties"

Air Products Incorporated, Allentown, PA, January 1988
"Structurally Modified Polymers with Controllable Electronic and Ionic Properties"

Prof. Patty Wisian-Neilson from Southern Methodist University visited on February 19 and presented a talk entitled "Inorganic Polymers: Derivatives of Poly(alkyl/arylphosphazenes)."

END

DATE

FILMED

5-88

DTIC